rpc

RESEARCH AND PRODUCTIVITY COUNCIL

LE CONSEIL DE RECHERCHE ET DE PRODUCTIVITE

88-01560/

RESEARCH AND PRODUCTIVITY COUNCIL
College Hill Road
P.O. Box 6000
Fredericton, N.B.
E3B 5H1
Telephone 506-452-8994 Telex 014-46115

5-9195

CONTRACT REPORT NO OSQ85-00335

CIRCULATING FLUIDIZED BED GASIFICATION OF MINTO COAL AND N.B. OIL SHALE

Final Report

Submitted to
Allan Palmer
CANMET, Energy Research Laboratories
Dept. of Energy, Mines & Resources
555 Booth Street
Ottawa, Ontario
K1A 0G1

77 pp

JOB NO.: 05000227
REPORT NO.: AS/87/22
DSS FILE NO.: OSQ85-00335
DATE: January 5, 1987

R. Robson, Chemical Engineer
S.K. Barua, Process Engineer
P.F. Salib, Section Head
Fuel Technology

TABLE OF CONTENTS

	Page
SUMMARY	1
1.0 INTRODUCTION	2
2.0 THEORETICAL BACKGROUND	4
3.0 EXPERIMENTAL SET-UP	5
3.1 The Reactor	5
3.2 Stand Pipe	5
3.3 Primary Cyclones	5
3.4 The J-Valve	7
3.5 Condenser	7
3.6 The Secondary Cyclone	7
3.7 The Baghouse	7
3.8 Solid Feeding to the Reactor	7
3.9 Water/Steam Injection	8
3.10 Air Preheating	8
4.0 EXPERIMENTAL PROCEDURE	9
5.0 PREPARATION AND CHARACTERIZATION OF FEEDSTOCK	10
6.0 OPERATION EXPERIENCE	14
7.0 EXPERIMENTAL AND CALCULATED RESULTS	15
7.1 Overall Mass Balance	21
7.2 Nitrogen Balance	21
7.3 Carbon Balance	22
7.4 Oxygen Balance	22
7.5 Hydrogen Balance	22
7.6 Sulphur Balance	23
7.7 Ash Balance	23
8.0 ENERGY BALANCE	24
8.1 Thermal Efficiency	24
9.0 DISCUSSIONS	27
9.1 Effect of Steam	27
9.2 Effect of Temperature	28
9.3 Effect of Coal/Oil Shale Ratio	28
9.4 Effect of Air to Carbon Ratio	34
10.0 CONCLUSIONS	36
11.0 RECOMMENDATION	38
12.0 REFERENCES	40

13.0 AUTHORIZATION 41

14.0 APPENDICES 42

Appendix 1 - Progress Report No. 1 42

Appendix 2 - Results of Chemical Analysis 66

Appendix 3 - Summary of Weekly Activities 69

Apendix 4 - Typical Gas Chromatograph Tracing 74

TABLES

1 Sieve Analyses of Shale Fines and Coal 11

2 Chemical Analyses of Oil Shales and Minto Coal 12

3 Fischer Assay Analyses of Oil Shale and Minto Coal 13

4 Accumulation Char in the Standpipe 71

5 Summary of Experimental Conditions and Results 16

6 Overall Mass Balance for the Gasification of Minto Coal and N.B. Oil Shale 17

7 Elemental Mass Balance 18

8 Ash Balance 19

9 Elemental Mass Balance Percentage Errors 20

10 Energy Balances for the Gasification of Minto Coal and N.B. Oil Shale 26

FIGURES

1 Schematic of RPC Circulating Fluidized Bed Gasifier System 6

2 Effect of Mix Ratio on the Gross Calorific Value of the Product Gas 30

3 Effect of Oil Shale Feedrate on the Gross Calorific Value of the Product Gas 31

4 Effect of Mix Ratio on the Production of Methane 32

5 Effect of Mix Ratio on the Reduction of Sulphur in the Product Gas 33

6 Effect of Air to Carbon Ratio on the Conversion of Carbon to Gaseous Products 35

SUMMARY

This is the final report for DSS Contract NO.: 03SQ85-00335, the requirement being the "Pyrolysis of New Brunswick Oil Shale and Coal in a Circulating Fluidized Bed". The objectives were to assess the potential of the RPC novel pyrolysis scheme in which the combustion of the product char and pyrolysis of the fresh feed took place in alternate cycles. The feedstock to be tested was a mixture of New Brunswick oil shale and high sulphur Minto coal.

The pyrolysis program was not as successful as anticipated due to difficulties in controlling the operating parameters. As a result, the pyrolysis cycle could not be sustained for an extended period of time and no oil was generated. The report on the pyrolysis program "Pyrolysis of New Brunswick Oil Shale and Coal in a Circuating Fluidized Bed" is attached in the Appendix 1.

After consultation with the Scientific Authority, efforts were directed towards the gasification of Minto coal and N.B. oil shale. The objectives were to optimize the gas quality and sulphur capture by the oil shale.

The reactor system was operated reliably with the Minto coal and oil shale under a wide range of operating conditions. The calorific value of the gas ranged from 0.44 to 0.95 MJ/m^3. The former was obtained with coal only, while the latter with 1:3 coal-oil shale mix. Corresponding sulphur capture ranged varied from 0% to 71%. None of the independent variables investigated, except the ratio of coal-oil shale mix shown any significant effect on the gas quality. The calorific value of the gas was found to increase with the increase in the proportion of oil shale in the feed. Similar trend was also observed for sulphur capture.

1.0 INTRODUCTION

This is the final report for the DSS Contract No. OSQ85-00335, the requirement being the "Pyrolysis of New Brunswick Oil Shale and Coal in a Circulating Fluidized Bed".

The project involved the assessment of the Research and Productivity Council's (RPC) novel pyrolysis scheme where Minto coal and oil shale mixture is first pyrolyzed followed by the combustion of product char in the same reactor. Heat generated during the combustion provides the energy for the pyrolysis part of the cycle. These two distinct processes were to be carried out in alternate cycles. Completion of one process cycle is followed by the initiation of the other.

A number of problems were encountered during the experimental phase of the program. The unsteady nature of the process, especially the pyrolysis cycle, made the control of different recycled gas streams very difficult. These gas streams were used to replace the air streams of combustion cycle. A steady flow of these gaseous streams is a pre-requisite for a reliable operation of the system. Sometimes, it was difficult to initiate the pyrolysis cycle. Whenever the pyrolysis cycle was successfully initiated, it could not be sustained for any significant length of time, resulting in little or no oil recovery. The program was terminated when these technical problems could not be resolved satisfactorily to improve the oil yield. The results of this investigation have been reported in the RPC Progress Report No. AS/87/12. A copy of the report is attached in the Appendix 1.

After consultation with the Scientific Authority, the objectives of the program were changed. It was decided to direct the efforts towards the gasification of Minto coal and oil shale mix to produce a low calorific gas. The effects of different independent process variables on the quality of gas were to be investigated. This report gives an account of the experimental work, results and discussions conclusions and recommendations for further work.

Gasification of coal to produce a low calorific value gas is an important future option for the industrial users, particularly the utility companies. Low calorific value gas, when used for power generation, offers the best economic option (1, 2). In terms of technology, it offers the utility with the possibility of adding capacity of small increments in the range of 10-100 MWe. Direct combustion based generating methods become less efficient with a decreasing scale.

2.0 THEORETICAL BACKGROUND

The gasification of carbonaceous material can be represented by five basic chemical reactions (3):

a) combustion: $C+O_2 \rightarrow CO_2$, $\triangle H = -405.9$ kJ/mol

b) partial combustion: $C+\frac{1}{2}\ O_2 \rightarrow CO$, $\triangle H$ -123.1 KJ/mol

c) boudouard reaction: $C + CO_2 \rightarrow 2CO$, $\triangle H = 159.7$ KJ/mol

d) water-gas reaction: $C+2H_2O \rightarrow CO + H_2$, $\triangle H = 118.9$ KJ/mol
(steam-carbon reaction)

e) hydro-gasification reaction:

$C+2H_2 \rightarrow CH_4$, $\triangle H = -87.4$ KJ/mol

The shift reactions, given below, is of importance to adjust the CO/H_2 ratio in the gas mixture.

f) $CO+H_2O \rightarrow CO_2+H_2$ $\triangle H = -40.9$ KJ/mol
An increase in calorific value can be achieved by methanation.

g) $CO+3H_2 \rightarrow CH_4+ H_2O$, $\triangle H = -206.3$ KJ/mol

Thermodynamically, the Boudouard and steam-carbon reactions which are important for gasification are favoured at higher temperatures. An increase in pressure will drive these two reactions towards the starting material. Since RPC's circulating fluidized bed was designed for atmospheric pressure and relatively high temperature, it was assumed that these two reactions will proceed to a significant degree. The prevailing temperature and pressure in an atmospheric circulating fluidized bed is not thermodynamically conducive to drive the reactions e), f) and g) towards the right. It was hoped that the advantages gained from the Boudouard and steam carbon reactions would be sufficient to achieve the necesssary carbon conversion.

3.0 EXPERIMENTAL SET-UP

The circulating fluidized bed reactor system is shown schematically in Figure 1. It consists of a circulating fluidized bed, a primary cyclone, a stand pipe, a packed bed condenser, a secondary cyclone and a baghouse. Solids are fed to the system pneumatically. Either steam or hot water can be injected into the system as necessary. A brief description of the major components is given below.

3.1 The Reactor

The combustor is cylindrical in shape with a total height of 5.8 m (19') with an inside and outside diameter of 12.7 cm (5") and 50.8 cm (20"), respectively. The wall consists of three layers of material: the inner layer made up of high temperature refractory, a middle layer of castable insulating refractory, and a carbon steel shell. The thickness of the high temperature refractory and insulating are 5 cm and 13 cm, respectively. A 0.5 million Btu propane burner is used for start-up purposes.

3.2 Stand Pipe

The stand pipe is used for storage and recirculation of hot solids received from the primary cyclone. It is 2.7 m (9') high and has an inside and outside diameter of 22.8 cm (9") and 61 cm (24") respectively. The stand pipe is also refractory lined and it is also equipped with discharge and sampling ports.

3.3 Primary Cyclones

The primary cyclone which is 30 cm (12") in diameter, is refractory lined in a similar manner to the reactor and the standpipe.

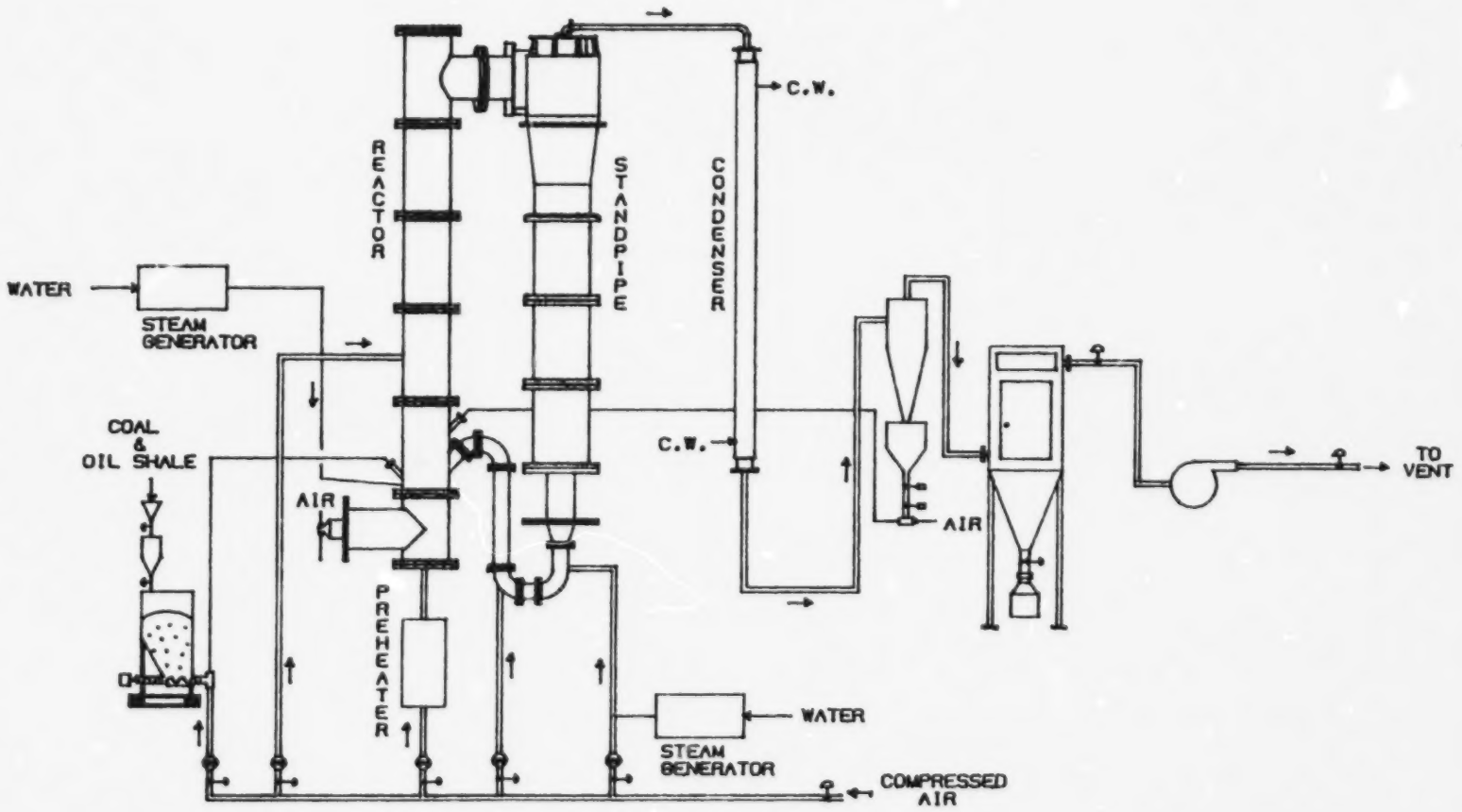


FIGURE 1 : SCHEMATIC OF RPC CIRCULATING FLUIDIZED BED GASIFIER SYSTEM

3.4 The J-Valve

Circulation of solids from the standpipe to the reactor is achieved by the non-mechanical J-valve. Air/steam is supplied at two points - one at the base of the standpipe, and the other is at the base of the vertical section of the J-valve. The J-valve is made of 2", Schedule 40, SS pipe.

3.5 Condenser

The gases were cooled in a water cooled one pass heat exchanger which is made of two concentric pipes of a nominal diameter of 15 cm (6") (Schedule 40) and 20 cm (8") (Schedule 60), respectively. The height of the exchanger is 5.2 m (17").

3.6 The Secondary Cyclone

The secondary cyclone is 25 cm in diameter and made of 304 SS stainless steel. Since the operating temperature is low, the cyclone is neither insulated or refractory lined.

3.7 The Baghouse

The flue gases from the cooling section are fed through the secondary cyclone into the baghouse. The latter is a continuous duty self cleaning dust collector which consist of 16 high temperature bags capable of handling 200 SCFM.

3.8 Solid Feeding to the Reactor

Two screwfeeders were available to feed the solids. One was used for feeding the fresh solid and the other for recycling the solids from the secondary cyclone.

The solids, discharged by the screw feeder from the storage bin, were entrained by air and fed into the reactor. The storage bins and the screwfeeders are placed on load cells to provide an account of the solid feed rates.

3.9 Water/Steam Injection

Two water heaters are provided to supply hot water/steam as necessary for gasification. One is connected to the aeration part of the J-valve, the other part close to the distributor plate. Most of the water requirement was introduced as steam just above the distributor plate. A constant amount of 40 ml of water at room temperature is introduced in the J-valve as aeration fluid along with the air. The water heaters were made by wrapping heating coils around a pipe.

3.10 Air Preheating

An electrical air preheater was installed to heat the primary air up to 450^{o}C. This preheater was activated whenever it was necessary. Air preheating was not necessary when only coal was gasified. Gasification of 1:2 and 1:3 coal-oil shale mix need air preheating to have the desired temperature in the reactor.

4.0 EXPERIMENTAL PROCEDURE

The reactor was preheated to a temperature of 620°C using the 0.5 million Btu/hr propane burner. This temperature was reached after about 16 hours. The burner was then shut off and coal was fed into the reactor. The bed temperature rose steadily as the coal combusted. When the reactor temperature was above 800°C, steam was injected. The reactor was operated for sufficient time to achieve stable operating conditions. The operating variables were then set for any particular run. This procedure takes about 24 hours from start of the preheating.

Although all the dependent and independent variables were continuously monitored readings were only recorded every hour. The readings include: coal/oil shale feed, air and steam/water flow rates, temperature at different locations of the system, the composition of the flue gas, solid discharge rates and the secondary cyclone solid recycle rates. These data are sufficient for complete heat and mass balance assessments for the system.

5.0 PREPARATION AND CHARACTERIZATION OF FEEDSTOCK

As-received oil shale and coal were oven dried to remove excess surface moisture. The dried shale was screened through 1/8" screen to reject the fines. The oversize fraction retained on 1/8" screen were crushed in a jaw crusher and screened.

The dried coal was first crushed in a jaw crusher and then in a cone crusher. No further screening of the crushed coal were made. The size analysis, ultimate, proximate and ash analysis and the Fischer assay are shown in Tables 1, 2 and 3.

TABLE 1

Sieve Analysis of Shale

Fines and Coal

Screen Size Mesh	Weight % Shale	Weight % Coal
+9	12.6	36.1
-9+24	46.6	26.4
-24+42	17.0	16.8
-42+80	8.2	11.9
-80	15.6	8.5

TABLE 2

Chemical Analyses of Oil Shales and Minto Coal

	N.B. Shale	Minto Coal
Proximate Analysis (wt%)		
Moisture	1.74	0.46
Ash	79.50	15.24
Volatile Matter	18.50	36.0
Ultimate Analysis (wt%)		
Carbon - Organic	10.38	69.76
Inorganic	0.76	-
Hydrogen	1.81	4.82
Nitrogen	0.45	0.97
Oxygen (by difference)	5.05	2.83
Sulphur	0.31	5.92
Ash Analysis (wt%)		
SiO_2	67.3	28.8
Al_2O_3	15.99	19.3
CaO	3.78	0.37
MgO	1.84	0.26
Fe_2O_3	4.64	48.7
Na_2O	2.00	0.41
K_2O	2.05	0.60
Calorific Value (Btu/lb)	2026	13081

TABLE 3
Fischer Assay Analyses of
Oil Shale and Minto Coal

	Oil Shale	Minto Coal
% Oil Yield	3.9	2.6
% Gas Lost	6.6	1.3
% Water Yield	2.5	1.1
Oil Yield (Imp Gal/Ton	8.9	5.6
Oil Density (g/cc at 15.5°C)	0.870	0.919

6.0 OPERATING EXPERIENCE

The gasifier was operational for a total of 32 days spread over an eight week period. The first five weeks were spent debugging the system so that it could be operated reliably for an extended period of time. Detail activities on a weekly basis are summarized in the Appendix 3.

The problems encountered resulted from the equipment malfunction and operational difficulties. The equipment malfunction was relatively easy to detect and correct. The operational problem such as slugging, feed disruption and an unreliable solid recycling were difficult to resolve and needed a thorough investigation before arriving at a satisfactory solution. Some of the operational problems were interdependent, such as, an increase in the pressure in the system for any reason eventually will disrupt the feed and also will lead to an unreliable solid recycle. Slugging, which is an undesirable phenomena, reduces not only the heat and mass transfer rates, but also disrupts solid feeding.

All these problems were systematically resolved resulting in a reliable operation of the system for an extended period of time. Some of the important findings are:

- Minimum operating velocity in the reactor must be 23 ft/sec or more at 850°C.

- Since the recycling solid is rich in carbon, water had to be injected with the air for the operation of J-valve to avoid the formation of clinker. Water or steam alone, instead of air did not perform satisfactorily for a reliable operation of the J-valve.

7.0 EXPERIMENTAL AND CALCULATED RESULTS

A total of eleven runs were carried out. Run No 1 to 5 were performed with Minto coal only. The remaining runs were made with a mix of Minto coal and oil shale. The duration of the coal runs ranged from 6 to 15 hours, while the coal- oil shale mix runs were continued for a minimum of 12 hours except for one run, which lasted for 10 hours.

The experimental conditions and results of all the experimental runs are summarized in Table 5. The process performance, evaluated in terms of mass and energy balances and the thermal efficiency, is discussed below. Overall mass balance, elemental balance, ash balances and elemental balance errors are shown in Tables 6, 7, 8 and 9 respectively. All the analytical results are given in Appendix 2.

TABLE 5
Summary of Experimental
Conditions and Results

Run #	Feed Rate Kg/hr	Air/Carbon Ratio (w/w)	Water/Carbon Ratio (molar)	Coal/Oil Shale Ratio (w/w)	Reactor Temp. Exit ^{o}C	Dry Gas Analysis H_2%	O_2%	CO_2%	CO%	SO_2(ppm)	CH_4%	Gross Gas Heating Value (MJ/M^3)	Thermal Efficiency %	Carbon Conv. %	Sulfur Red. %
1	14.0	9.97	0.478	1:0	855	0.6	0.34	16.0	2.46	7020	0.20	0.443	39.1	78.0	7.71
2	13.5	10.51	0.722	1:0	859	0.6	0.48	15.9	2.04	7440	0.40	0.468	44.9	79.5	-1.5
3	14.0	9.74	0.949	1:0	840	0.7	0.04	15.6	2.23	5560	0.22	0.435	42.4	73.8	28.4
4	14.9	9.48	0.892	1:0	845	1.0	0.11	16.2	2.54	5990	0.60	0.652	47.6	75.1	26.9
5	27.0	8.97	0.945	1:1	839	1.1	0.07	15.9	3.06	3780	0.58	0.719	48.5	70.8	53.0
6	26.8	8.86	0.735	1:1	853	1.0	0.27	15.7	3.10	3070	0.50	0.682	45.5	70.8	61.3
7	27.2	8.92	1.13	1:1	846	1.0	0.12	15.8	3.14	3040	0.50	0.686	48.7	72.7	60.9
8	34.9	9.09	0.982	1:2	828	1.28	0.06	15.5	3.24	2110	0.78	0.838	51.7	71.0	71.6
9	42.1	9.16	0.982	1:3	818	1.0	0.10	15.0	2.70	2500	1.4	0.973	51.9	72.6	62.6
10	26.6	8.91	0.959	1:1	808	0.81	0.08	15.0	3.13	4660	0.52	0.670	47.1	68.4	41.2
11	26.0	9.17	0.776	1:1	896	1.35	0.11	15.9	2.25	3410	0.66	0.682	49.5	73.8	53.9

TABLE 6

Overall Mass Balance For The
Gasification of Minto Coal
and N.B. Oil Shale

	INPUTS				OUTPUTS						
	Coal	Oil Shale	Air	Water	Secondary Cyclone Discharge	Baghouse Discharge	Standpipe Discharge	Product Gas, Wet (by difference)	Dry Product Gas	Water In Product Gas	Recycle Condenser Solids
Run#	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	Kg/hr
1	14.0	-	97.4	6.9	4.40	0.60	-	113.3	104.2	9.10	5.20
2	13.5	-	99.0	10.1	4.30	0.92	-	117.4	104.2*	13.2	6.38
3	14.0	-	95.1	13.8	4.78	0.52	0.42	117.2	101.5	15.7	4.90
4	14.9	-	98.5	13.8	4.58	0.33	-	122.3	102.3	20.0	5.64
5	13.5	13.5	97.1	15.0	7.49	0.61	7.36	123.6	99.1	24.5	8.48
6	13.4	13.4	95.2	11.5	7.87	0.55	6.03	119.1	99.5	19.6	8.58
7	13.6	13.6	97.2	18.2	7.67	1.18	5.79	128.0	103.0	25.0	6.63
8	11.6	23.3	95.5	15.0	9.91	1.85	10.8	122.8	95.9	26.9	10.3
9	10.5	31.6	97.1	15.0	9.25	2.01	18.2	124.7	100.9*	23.8	6.05
10	13.3	13.3	95.0	15.0	7.69	1.53	5.07	122.3	98.9	23.4	5.99
11	13.0	13.0	95.5	11.8	7.54	1.29	0.64	123.8	103.2	20.6	8.70

* determined using a nitrogen balance

other dry gas flows determined by measuring the moisture in the product gas

TABLE 7

Elemental Mass Balance

	INPUTS, Kg/hr					OUTPUTS, Kg/hr				
Run #	Nitrogen	Oxygen	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Carbon	Hydrogen	Sulphur
1	74.84	29.28	9.766	1.452	0.8288	75.90	27.96	10.05	1.116	1.0133
2	76.06	32.48	9.418	1.785	0.7992	76.06*	31.49	9.795	1.604	0.8836
3	73.08	34.87	9.766	2.222	0.8288	75.22	32.40	9.356	1.869	0.6576
4	75.69	35.69	10.39	2.266	0.8821	74.21	37.33	10.09	2.407	0.7397
5	74.67	37.28	10.82	2.602	0.8411	72.23	40.46	10.14	2.939	0.5423
6	73.21	33.72	10.74	2.205	0.8348	72.78	36.13	10.17	2.368	0.5014
7	74.75	40.15	10.90	2.966	0.8473	75.32	41.55	10.11	3.338	0.4819
8	73.47	37.49	10.51	2.706	0.7590	70.40	41.60	10.16	3.256	0.4240
9	74.72	38.37	10.60	2.819	0.7196	74.72*	39.17	10.30	2.996	0.5702
10	73.05	36.77	10.66	2.589	0.8286	73.21	38.62	9.88	2.787	0.6646
11	73.43	34.01	10.42	2.211	0.8099	75.96	37.33	8.97	2.509	0.4811

* nitrogen output was forced to equal nitrogen input

TABLE 8
Ash Balance

Run #	Ash In Kg/hr	Ash Out Kg/hr	In-Out x 100 % Error
1	2.13	2.25	- 5.62
2	2.05	2.75	-34.0
3	2.13	3.40	-59.6
4	2.27	2.46	-8.67
5	12.79	13.01	-1.72
6	12.70	11.92	6.14
7	12.88	12.46	3.26
8	20.29	19.97	1.58
9	26.72	26.99	-1.01
10	12.60	11.85	5.95
11	12.32	8.29	32.7

TABLE 9

Elemental Mass Balance

Percentage Errors*

Run #	Nitrogen	Oxygen	Carbon	Hydrogen	Sulphur
1	-1.42	4.51	-2.91	23.1	-22.3
2	0.00**	3.05	-4.00	10.1	-10.6
3	-2.93	7.08	4.20	15.9	20.7
4	1.96	-4.60	2.89	- 6.22	16.1
5	3.27	-8.53	6.28	-12.9	35.5
6	0.59	-7.15	5.31	- 7.39	39.9
7	-0.76	-3.49	7.25	-12.5	43.1
8	4.18	-11.0	3.33	-20.3	44.1
9	0.00**	-1.82	2.83	- 6.28	26.2
10	-0.22	-5.03	7.32	- 7.65	19.8
11	-3.45	-9.76	13.9	-13.5	40.6

* Percentage error = $\frac{\text{IN-OUT}}{\text{IN}} \times 100\%$

** no error in the nitrogen balance since nitrogen output was forced to equal nitrogen input

7.1 Overall Mass Balance

All input and output streams, flowrates and compositions were measured except for the total product gas flowrate. Therefore the flowrate of the product gas was determined by closing the overall mass balance. The composition of the dry product gas was determined using the continuous gas analysis and periodic gas chromotography. The percentage moisture in the product gas was determined for all runs except 2 and 9. To determine the flowrate of dry gas for these two runs, nitrogen was used as a tie component.

7.2 Nitrogen Balance

Nitrogen balanced well for all runs. The average discrepancy in the nitrogen balance was $0.14 \pm 2.63\%$. It is expected that the error in the nitrogen balance would be low since the amount of nitrogen entering and leaving the reactor is large.

7.3 Carbon Balance

The carbon balance error for all the tests was good with the average being $4.22 \pm 4.90\%$. This indicates that, on the average more carbon is reported entering than leaving the reactor.

Carbon entering the reactor is in two forms; as a fresh feed and the secondary cyclone recycle. The majority of the carbon (75%) leaving is in a gaseous state and the rest is unreacted in the solid discharge from the secondary cyclone, baghouse and standpipe. Since the flowrates and carbon content of the solids can be measured quite accurately, the error likely occurs in the gas measurement. The dry gas composition is measured both with continuous gas analyzers and by gas chromotography and as is considered to be accurate. However, the flowrate of dry product gas is

directly related to the measurement of the moisture in the gas. The flowrate of wet product gas is found from an overall mass balance and the total amount of water in the product gas is not measured but only the percentage. Any error in the water leaving the reactor causes a corresponding error in the total dry product gas flow rate. From the errors in the oxygen and hydrogen mass balances discussed below it appears that the calculated flowrate of water exiting the reactor was too large. Therefore the calculated flow rate of dry product gas would be lower than actual. This would lower the total amount of carbon leaving the reactor and could account for the error in the carbon balances.

7.4 Oxygen Balance

The average error in the oxygen balance was -3.34 $\pm$ 6.0%. The oxygen balance is very sensitive to inaccuracy in measurements of the water output from the reactor since much of the oxygen is water bound. For the majority of the runs, more oxygen was determined to be leaving the reactor than entering. This could indicate that the experimental method used to determine the percentage moisture content in the gas resulted in values that were too large. This is support by the fact that the oxygen balance error is low for runs 2 and 9 where the water content in the product gas was not measured but was determined from a nitrogen balance.

7.5 Hydrogen Balance

The hydrogen balance like the oxygen balance is very sensitive to the water output measurement since the marjority of the hydrogen is contained in the form of water. As with the oxygen balance for most runs more hydrogen is reported leaving the reactor than entering. Again inaccuracies in the measurement of the water content in the product gas could be the cause.

7.6 Sulphur Balance

The error in the sulphur balances was the highest among the various elements. The average error was 23.0 ± 22.0%. This is most probably due to accumulation of sulphur within the bed inventory.

7.7 Ash Balance

Table 8 shows that, Run No 1 to 5, which were made with Minto coal, total ash leaving is larger than the ash input to the system, while, for runs (5 to 11) using coal and oil shale mix the reverse is true. The anomaly could be explained as follows:

Material is discharged from the system through standpipe overflow, secondary cyclone discharge and baghouse discharge. Standpipe discharge occurs when the level of material in the standpipe rises above the overflow port and is used to prevent accumulation of material in the system. Secondary cyclone discharge and baghouse discharge is a very fine material which is ellutriated from the primary cyclone and can occur regardless of the amount of material in the system. If the rate of ash entering the reactor in the fuel is less than the rate of ellutriation then there will be a net loss of material and this will be reflected in the ash balance error. This is the case when feeding Minto coal which has low ash (15%). When oil shale is fed the amount of ash is much greater as shown in Table 8 runs 5 to 11. In this case the ash fed is much larger than the ellutriation rate and large standpipe overflow and good ash balances are obtained.

8.0 ENERGY BALANCE

The energy balance was calculated based on the heat content of the inputs (coal, oil shale, air and steam) and the outputs (sensible and heating value of dry product gas and solids, and heat content of the steam). Heat losses were considered to be the difference between the input and output streams. The results are presented in Table 10.

The average calculated heat loss in the system was 32.6% which is large but not entirely unexpected due to the large surface area to volume ratio characteristic of all small reactors. This is especially true for this circulating fluidized bed reactor system which has a large standpipe containing inert solids.

In a large scale unit the surface area to volume ratio would be decreased considerably since the volume (thermal output) is proportional to the square of the diameter while the surface area (heat loss) is proportional to the diameter.

8.1 Thermal Efficiency

The thermal efficiency of the gasifier is the measurement of the efficiency of the recovery of useful energy from the coal and oilshale. In this case useful energy will be defined as heat recoverable from the product gases whereas the heat contained in the solids discharge will be considered a loss or unrecoverable. Therefore the thermal efficiency is:

$$\text{Thermal efficiency} = \frac{\text{heat content of hot wet gas}}{\text{total heat input}}$$

The heat content of the hot wet gas is the summation of the sensible heat of the wet product gas and the heat of combustion of the product gas. The thermal efficiency for these tests ranged from 39.1% to 51.9% and are shown in Table 5.

However from Table 10 it can be seen that the majority of the heat content in the product gas is in the form of sensible heat in the dry gas and heat in the steam. The heating values of the dry gas are low and contribute little to the overall efficiency of the process (7.5% - 15%).

TABLE 10

Energy Balances for the Gasification of Minto Coal and N.B. Oil Shale

Run #	INPUTS (KJ/hr)					OUTPUTS (KJ/hr)								
	Coal	Oil Shale	Air	Water	Total In	Secondary Cyclone	Baghouse	Standpipe	Recycle	Combustion Gas (Dry) sensible heat	Combustion Gas (Dry) calorific value	Water	Total Out	% Loss
1	425951	-	517	12046	438514	84756	9421	-	5542	97510	35590	38560	271379	38.1
2	410739	-	526	17384	428649	69854	14558	-	7128	98566	37631	56059	283796	33.8
3	425951	-	505	30054	456510	71416	8227	348	5131	93365	34083	65963	278533	39.0
4	453334	-	524	30054	483912	80294	5600	-	6188	94597	51713	83987	322379	33.4
5	410739	63616	9836	33166	517357	65088	4564	26502	7935	92495	55508	102884	354976	31.4
6	407696	63144	9723	24053	504616	56649	3631	27765	7919	93779	52858	82958	325559	35.5
7	413781	64087	13926	34771	526565	56892	5790	20647	6086	96210	55085	105397	346107	34.3
8	352931	109796	13455	33165	509347	53133	7576	50769	8811	88113	63011	112258	383671	24.7
9	319464	148908	13748	33165	515285	34216	5743	71553	5043	91777	77141	98758	384231	25.4
10	404654	62673	504	33165	500996	56863	8232	43066	5157	87608	51653	96545	349124	30.3
11	395526	61260	13417	24084	494287	44737	6926	1657	8296	101144	55050	88520	306330	38.0

9.0 DISCUSSIONS

The experimental program was aimed at identifying the effect and significance of the various operating parameters in determining the quality of the produced gas. The effects of these parameters on the quality of gas and on the process performance are discussed below:

9.1 Effect of Steam

Steam was found to have no effect on the gas composition when gasifying Minto coal alone or mixtures of Minto coal and New Brunswick oil shale. Water to carbon molar ratios ranging from 0.471 to 1.13 were used in runs 1 to 11 as shown in Table 5. In runs 1 to 3 Minto coal was gasified at essentially constant operating conditions except for the water to carbon molar ratio which varied from 0.478 to 0.949. The product gases were essentially the same in composition and heating value. 0.435 - 0.468MJ/m^3 (11.7 - 12.6 Btu/Ft^3).

In runs 5 to 7 a mixture of Minto coal and New Brunswick oil shale (1:1 by weight) was gasified at varying water to carbon molar ratios (0.714 to 1.11). As with coal there was little change in product gas composition and heating value (6.682 - 0.719 MJ/m^3).

For all the tests, the amount of water in the product gas was greater than the amount of steam fed into the reactor (see Table 6) which indicates that no net decomposition of steam has occurred. In all cases the amount of hydrogen contained in the product gas in the form of H_2 and CH_4 was much less than the hydrogen available in the coal and oilshale. These two facts indicate that the carbon-steam reaction was not significant in the formation of H_2 or CO.

9.2 Effect of Temperature

The effect of temperature was investigated by gasifying a 1:1 by weight mixture of coal and oil shale at three reaction temperatures of 808°C, 853°C and 896°C. There was virtually no change in the gross heating value of the gases produced (0.682 MJ/m^3). However there was a slight effect on the composition of the product gas. Increasing the reactor temperature from 808°C to 896°C increased the percentage of H_2 in the gas from 0.81% to 1.35% and decreased the amount of CO from 3.13% to 2.25%.

9.3 Effect of Coal/Oil Shale Ratio

Three different mixtures of Minto coal and N.B. oil shale were tested in runs 5 to 9 as shown in Table 5. It was intended to maintain all operating parameters constant from one test to the next in order to assess the effect of mix ratio. However as can be seen in Table 5 the temperature in the reactor decreased as the ratio of coal to oil shale fed to the reactor decreased. This was a result of the large amount of ash (80%) contained in the oil shale which contributed no energy to the system but instead contributed to the heat loss from the system.

Additional energy was added to the system by preheating the air for the runs with 1:2 and 1:3 coal and oil shale mixtures. The heat added in the air, although small relative to the entire heat input into the system (see Table 10), was sufficient to maintain the desired reaction temperature (850°C) when feeding a 1:1 by weight mixture but was insufficient when feeding higher ratios of oil shale. However as mentioned above, the effect of temperature on the product gas was found to be minimal over the temperature range investigated in these tests. Therefore any change in the product gas is likely due to the change in mix ratio.

The mix ratio was found to be the only parameter which had any significant effect on the product gas. The heating value of the gas increased as the mass fraction of oilshale in the feed was increased as can be seen in Figure 2. Increasing the mass fraction of oilshale in the feed required a corresponding increase in the feed rate of oilshale in order to maintain constant air to carbon ratios on weight basis. The gas gross calorific value was found to be a linear function of the oilshale feed rate as shown in Figure 3. The main contribution to the increase in heating value was found to be from methane which has a heating value more than three times that of hydrogon on carbon monoxide on a volume basis. The additional methane is provided by the oilshale since increasing the proportion of oilshale in the feed corresponds to an increase in methane production as shown in Figure 4.

Gas chromatrography was used to determine the percentages of hydrogen, methane and ethane present in the product gases. Table 5 did not report any values for ethane since for coal, the amount was considered only very minimal. For coal-oil shale mixture also, the ethane was minimal. However, the chromatogram indicated the presence of other species that could not be identified but are thought to have been other C2+ gases. These would have contributed to the heating value of the product gases and made the effect of oil shale on heating value more pronounced.

Increasing the mass fraction of oil shale in the feed to the reactor also reduced the amount of SO_2 present in the product gas (see Figure 5). Previous studies at RPC on the combustion of coal and oil shale have shown the capabilities of oil shale to capture sulphur (4). This is due to the prescence of CaO contained in the oil shale ash; the calcium to sulphur molar ratio ranged from 0.291 (1:1 coal-oil shale mixture) to 0.872 (1:3 mixture). The Ca in the oil shale ash acts as a sulphur capture agent in the same way as limestone.

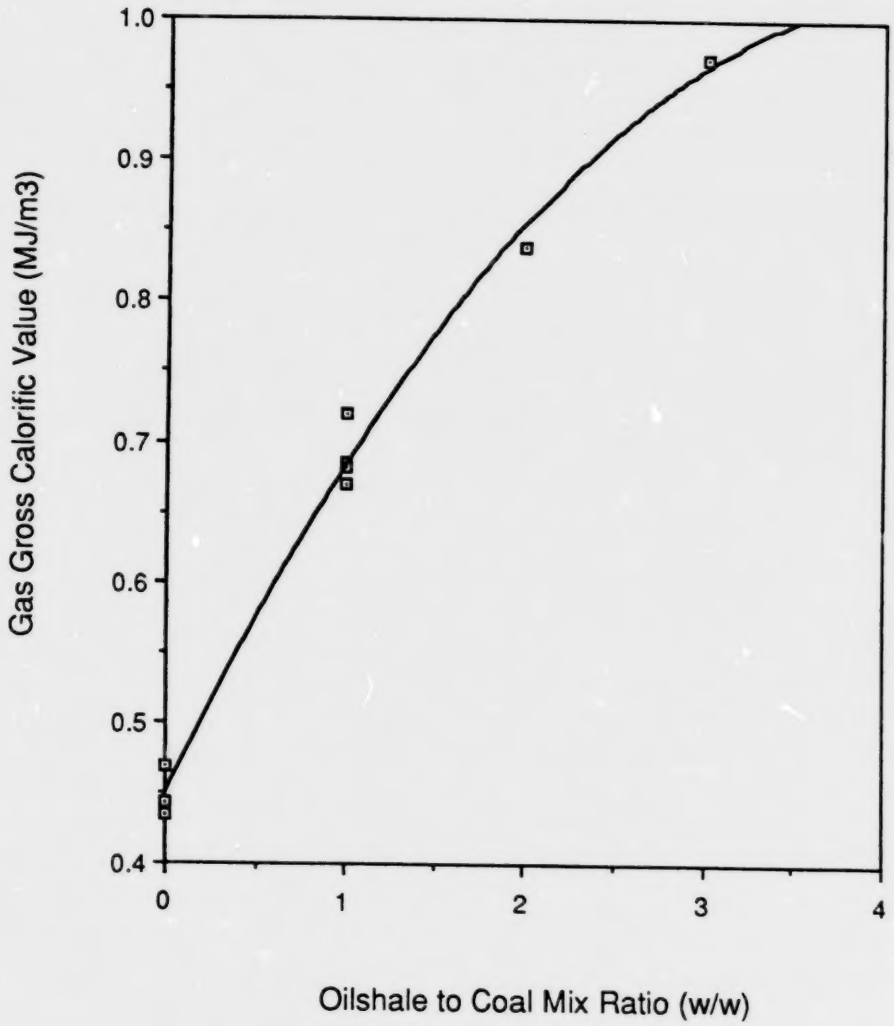


Figure 2: Effect of Mix Ratio on the Gross Calorific Value of the Product Gas

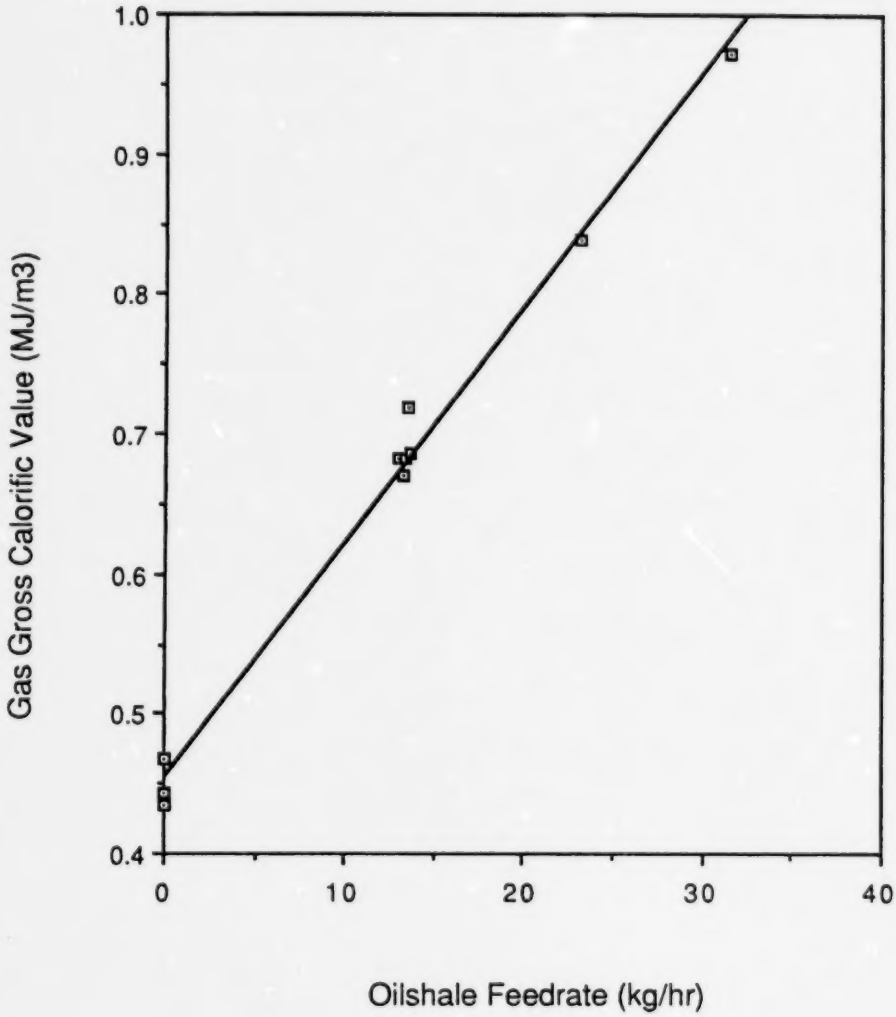


Figure 3: Effect of Oilshale Feedrate on the Gross Calorific Value of the Product Gas

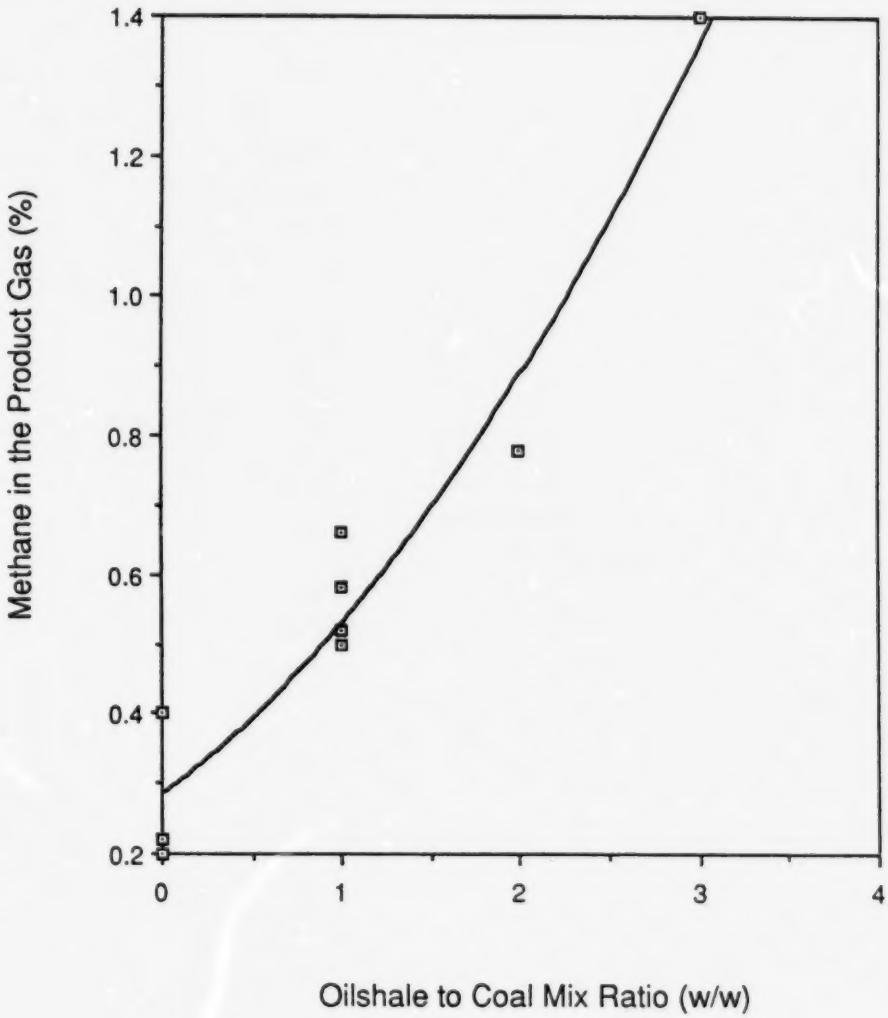


Figure 4: Effect of Mix Ratio on the Production of Methane

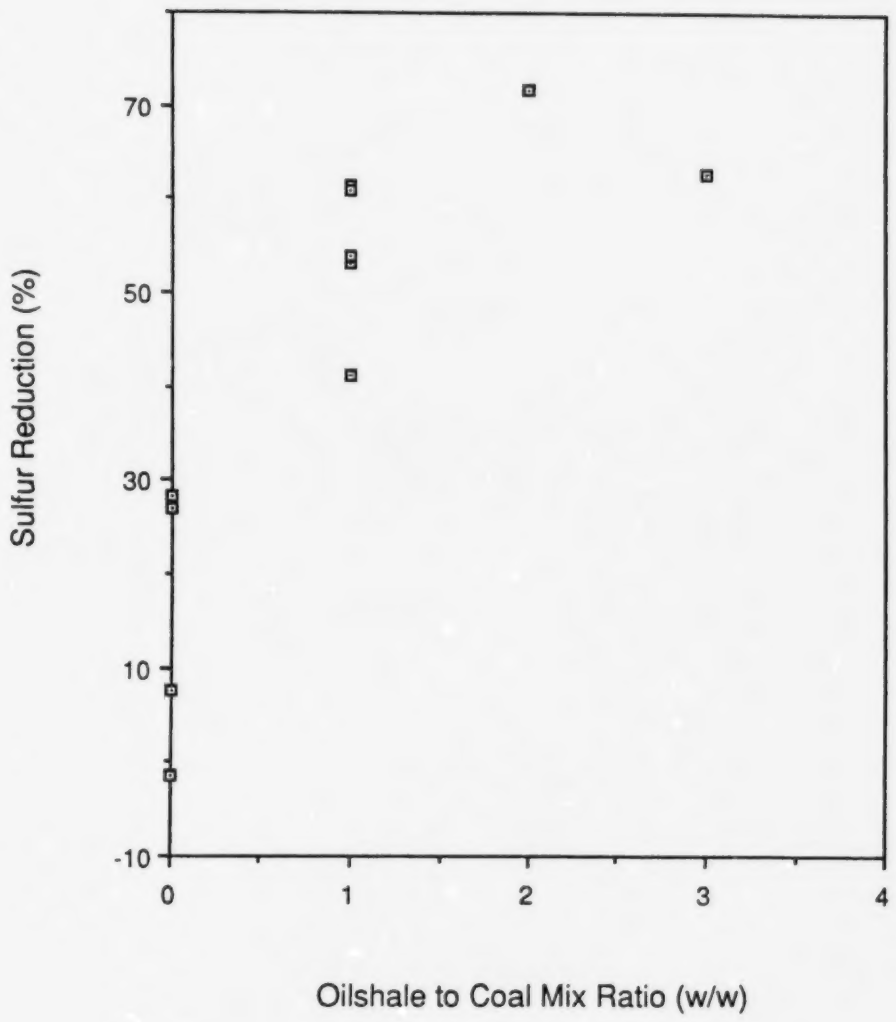


Figure 5: Effect of Mix Ratio on the Reduction of Sulfur in the Product Gas

9.4 Effect of Air to Carbon Ratio

The air to carbon ratio had a significant effect on the conversion of carbon in the feed to gaseous products. As the ratio of air to carbon was increased the efficiency of converting carbon to gaseous products (ie CO, CO_2, CH_4) increased. This is to be expected since it has already been determined that the steam-carbon reactions did not occur to any significant extent. (see effect of steam) Therefore the major reactions are combustion reactions which require oxygen. Increasing the air to carbon ratio provides the additional oxygen required to react with previously unconverted carbon.

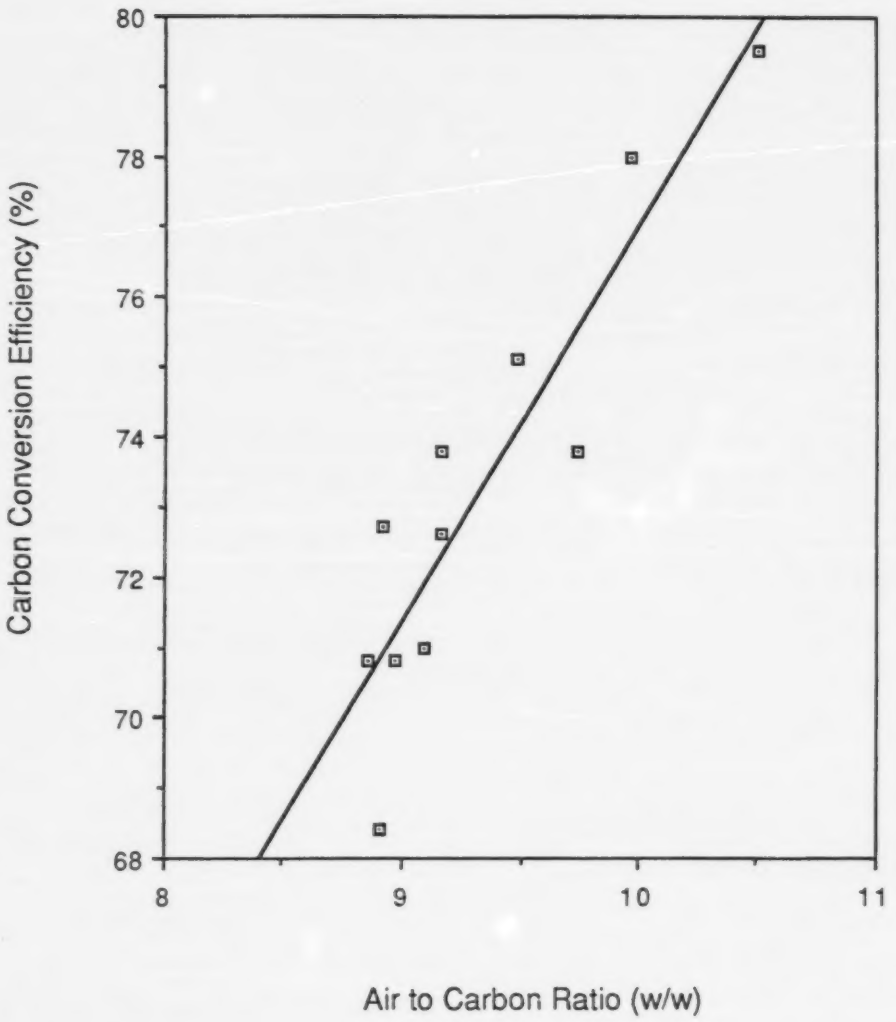


Figure 6: Effect of Air to Carbon Ratio on the Conversion of Carbon to Gaseous Products

10.0 CONCLUSIONS

Minto coal and N.B. oil shale were gasified in a circulating fluidized bed at various coal oil shale ratios, temperatures and steam flowrates. The calorific value of the gas produced was low (0.45 - 0.97 MJ//m^3). These values are much lower than the reported values of 3.8-7.6 MJ/m^3 for the gasification of coal with air.(3)

It was found that the steam-carbon reaction which, usually is one of the major sources of hydrogen and methane in a gasifier, did not occur to any significant degree in these tests. It is apparent from the composition of the gases produced that the major reactions occurring are combustion and partial combustion reactions. Essentially the reactor was operating as a combustor under reducing conditions. There was insufficient oxygen to react with the carbon and this carbon, instead of reacting with the water as expected, passed through the system and was ellutriated with the ash.

The major source of the carbon monoxide present in the product gas was most likely from the incomplete combustion of carbon with oxygen. (see section 2.0, reaction b)

Methane and most of the hydrogen were produced by pyrolysis reactions for both the coal and the oil shale. The higher methane production using oil shale is due to the difference in chemical structure between coal and oil shale. Coal consists of high molecular weight condensed aromatic structures low in hydrogen which are stable at the temperatures used in this study. Oil shale, however, consists of kerogen which has a higher hydrogen to carbon ratio than coal. The kerogen can be decomposed to gaseous products at the reactor temperatures of 800°C to 900°C.

The coal and oil shale could be processed together without operational problems such as clinkering of the solids in the reactor. However, there is a limit to the ratio of coal to oil shale that can be fed. The high ash content of oil shale is a burden on the system both in terms of solids handling and the maintenance of reactor temperature because of the associated heat loss by the ash. In the present system the 1:3 mixture of coal and oil shale was probably at the maximum. A larger unit would have lower shell losses and therefore, lower coal to oil shale ratios could be processed with a resulting improvement in product gas calorific value.

The oil shale ash was found to be beneficial in the reduction of SO_2 emissions because of the calcium oxide and magnesium oxide acting as sulphur capture agents.

In order to improve the calorific value of the gases produced it is necessary for the carbon-water reaction to proceed. The circulating fluidized bed reactor has high heat and mass transfer. Therefore the reason the carbon water reaction and not occuring is most likely due to kinetic limitations. That is, for the temperatures of 800-900^{o}C and residence times of the gases in this reactor, there is insufficient time and temperature for the carbon and water to react.

11.0 RECOMMENDATION

It is apparent from the results that the carbon steam reaction did not occur to any significant degree in the gasification tests performed. To improve the product gas calorific value requires the promotion of this reaction.

There are two possible approaches to this problem. One is to find a method that will increase the rate of the reaction, the other is to increase the contact time between the carbon and steam to allow for greater conversion.

Reaction temperature and pressure are known to have a dramatic effect on the rate of this reaction (5). Increasing the reactor temperature and pressure would greatly increase the reaction rate of carbon with steam. In the present system it was not possible to operate the circulating fluidized bed reactor above 900°C or at higher pressure because of limitation of the materials of construction. However, the capacity to operate at higher temperatures and pressures could be incorporated into future units.

Another possible method of increasing the reaction rate could be the use of a catalyst which would increase the reaction rate in the temperature range of 800°C to 900°C. However, either the catalyst must be inexpensive or an effective way of recovering it for reuse must be available.

To increase the contact time of the carbon and steam requires an increase in residence time of these components in the reactor. The carbon already has a greater residence time than the steam because of the high recycle of solid material and the refluxing of solids within the reactor. Therefore it is necessary to increase the steam residence time in the reactor. This could be accomplished by reducing the gas velocity and increasing the height of the reactor.

It was found that reducing the velocity in the present system was not feasible because of violent slugging of the solids in the reactor. Slugging at lower velocities would be greatly reduced in a larger unit where the wall effects on the flow of solids would be negligible. Also a larger unit could be taller to allow for greater gas residence time. However the effect of gas residence time on the overall conversion of carbon and steam to hydrogen and carbon monoxide would be far less than increasing the temperatuare and pressure. Only a marginal increase in conversion would occur. Since the increase in residence time would only be marginal and at best the amount of carbon converted would only be a linear function of reaction time. For example, if the carbon conversion was a linear function of reaction time and was doubled, the carbon conversion would also be doubled. Temperature and pressure, however are usually related exponentially to the reaction rate. Therefore, a small increase in temperature, for example, could dramatically increase the amount of carbon conversion.

Another approach to improving the gas calorific value could be to process a more reactive fuel source rather than Minto coal and oil shale. It has been reported in the literature that it is possible to successfully gasify low rank fuels such as lignite, wood and peat in a circulating fluidized bed. A gas calorific value of $6MJ/m^3$ from gasifying wood chips with air was reported by Lurgi in a CFB gasifier (6).

12.0 REFERENCES

1. Soriano, A.V., "Commercial Development of a Large Scale Coal Gasification System Designed to Produce Low Btu Gas"; Presented at the Eleventh Energy Technology Conference and Exposition, March 19-21, 1984; Washington, D.C.

2. Teper, M.; Hemming, D.F.; Ulrich, W.C., "The Economics of Gas from Coal", IEA Report by Economic Assessment Service, EAS Report E2/80, January, 1983.

3. Schilling, H.D., Bonn, B. and Krauss, U., "Coal Gasification Existing Processes and New Developments, pp10-31, Graham and Trotman, London, 1981.

4. Boorman, R.S., Salib, P., Gilders, R., and Gemmell, D.E., "Fluidized Bed Co-Combustion of Coal and Oil Shale a Route to SO_2 Emission Control", Can. Inst. Min., Proc. 3rd Meeting, Fredericton, N.B., 1982.

5. Grainger, L., Gibson, J., "Coal Utilization, Technology, Economics and Policy", pp 165, Graham and Trotman, London, 1981.

6 Lungi, "Wood Chip Fuel in a Circulating Fluid-Bed Gasifier", CPR1 Journal, pp 36-37, April/May 1986.

13.0 AUTHORIZATION

DEPARTMENT: APPLIED SCIENCES

PROJECT TITLE: CIRCULATING FLUIDIZED BED GASIFICATION OF MINTO COAL AND N.B. OIL SHALE

PROJECT NUMBER: 05000227 PROPOSAL NUMBER

REPORT AS/87/22

Prepared By: R. Robson
S.K. Barua

Reviewed By: P.F. Salib

Approved By: D. Abbott

Date: January 5, 1987

rpc RESEARCH AND PRODUCTIVITY COUNCIL
P.O. Box 6000, Fredericton, New Brunswick, Canada, E3B 5H1
Telephone (506) 452-8994
Telex 014-46115

APPENDIX 1

PROGRESS REPORT NO. 1

PYROLYSIS OF NEW BRUNSWICK OIL SHALE AND COAL IN A CIRCULATING FLUIDIZED BED

Progress Report No. 1

Dr. Edward Furmisky
CANMET, Energy Research Laboratories
Dept. of Energy, Mines and Resources
555 Booth Street
Ottawa, Ontario
K1A 0G1

JOB NO.: 05000227
REPORT NO.: AS/87/12
DSS FILE NO.:03SQ.23440-5-9195
DATE: July 4, 1986

S.K. Barua, Process Engineer
P. Salib, Head
Fuel Technology Section
R. Robson, Chemical Engineer
C. Ritchie, Chemical Engineer

TABLE OF CONTENTS

		Page
SUMMARY		i
1.0	INTRODUCTION	1
2.0	EXPERIMENTAL SET-UP	2
2.1	The Reactor	2
2.2	The Standpipe	4
2.3	Primary Cyclone	4
2.4	J-Valve	4
2.5	Combustion Cycle Off-Gas Cleaning	5
2.5.1	The Cooling System	5
2.5.2	The Secondary Cyclone	5
2.5.3	The Baghouse	5
2.6	Pyrolysis Cycle Off-Gas Cooling & Cleaning	5
2.6.1	Secondary Cyclone	5
2.6.2	Packed Bed Condensers	6
2.7	Solid Feeding to the Reactor	6
3.0	PREPARATION AND CHARACTERIZATION OF FEEDSTOCK	7
4.0	EXPLORATORY HOT TESTS	11
4.1	Experimental Procedure	11
4.2	Process Performance	11
4.3	Preliminary Gasification Tests	14
5.0	RECOMMENDATION FOR FUTURE WORK	15
5.1	Tentative Work Statement	15
5.2	Budget and Schedule	19
6.0	AUTHORIZATION	20

FIGURES

1	Schematic of RPC Cyclic Pyrolysis and Combustor System	3

TABLES

1	Sieve Analysis of Shale Fines and Coal	8
2	Chemical Analyses of Oil Shales and Minto Coal	9
3	Fischer Assay Analyses of Oil Shale and Minto Coal	10

SUMMARY

This is an interim report for DSS File No.: 03SQ.23440-5-9195, the requirement being the "Pyrolysis of New Brunswick Oil Shale and Coal in a Circulating Fluidized Bed". The objectives were to assess the potential of the RPC's novel pyrolysis scheme in which the combustion of the product char and pyrolysis of the fresh feed take place in alternate cycles. The feedstock to be tested is a mixture of New Brunswick oil shale and high sulphur Minto coal.

The system was operated for approximately 200 hours and a number of attempts were made to initiate the pyrolysis cycle. The maximum duration of the pyrolysis cycle was 43 minutes and the primary product was water mixed with char fines. No significant amount of oil was generated and the control of the different operating parameters was difficult.

Since the pyrolysis program was not as successful as anticipated, an alternate tentative test program for the gasification of mixtures of oil shale and high sulphur coal is given in this report. The objectives are to optimize the product gas quality and the sulfur capture by the oil shale.

1.0 INTRODUCTION

Coal pyrolysis is a thermal decompostion reaction in the absence of air at an elevated temperature to produce char and gaseous and liquid hydrocarbons. Since the char is a major product of pyrolysis, its effective utilization in an environmentally acceptable manner is necessary for the economic feasibility of the pyrolysis process. Consequently RPC's proposed pyrolysis concept based on a circulating fluidized bed, in addition to producing a liquid petroleum product, was to address carbon utilization as well as sulphur capture. In the proposed scheme, two distinct processes, namely pyrolysis of solid fuels and combustion of product char were to be carried out in the same reactor in two cycles. Completion of one process cycle was to be followed by the initiation of the other. Pyrolysis of solid fuels is to be carried out in one cycle producing a product char (in addition to liquid and gaseous hydrocarbons), which would then be combusted in the following cycle. Part of the heat generated in the combustion cycle is to be retained by the hot circulating solids and subsequently used to supply the heat requirements for the pyrolysis cycle. Cyclic operation is to be achieved by feeding air during the combustion cycle and replaced by the recycle gas during the pyrolysis cycle.

The feedstock for the test program is a mixture of New Brunswick high sulphur bituminous coal and New Brunswick oil shale. The latter contains calcium and magnesium carbonates which are known sulphur capture agents.

This progress report describes attempts to produce a liquid petroleum product.

2.0 EXPERIMENTAL SET-UP

The main reactor system consisted of a circulating fluidized bed reactor, a standpipe and a primary cyclone (Figure 1). Since the combustion and pyrolysis cycle produced gaseous products with different characteristics the off-gases were cleaned by two different cleaning trains. In the combustion cycle, the flue gases were first cooled by a water jacketed pipe followed by cleaning by a secondary cyclone and subsequently by a baghouse. In the pyrolysis cycle, the off-gases were cleaned by a secondary cyclone followed by condensation of the volatiles in two water-jacketed packed bed condensers placed in series. Initial experience with the pyrolysis condenser section showed that the packed bed condensers were plugged by the accumulated dust. The problem was resolved by spraying water at the top of the first condenser column so that the dust and water formed a sludge separate from the oil phase. The condensed oil and the sludge were to be collected at the bottom of the column.

2.1 The Reactor

The combustor is cylindrical in shape with a total height of 5.8 m (19') with an inside and outside diameter of 12.7 cm (5") and 50.8 cm (20"), respectively. The wall consists of three layers of material: the inner layer made up of high temperature refractory, a middle layer of castable insulating refractory, and a carbon steel shell. The thickness of the high temperature refractory and insulating are 5 cm and 13 cm, respectively. A 0.5 million Btu propane burner is used for start-up purposes.

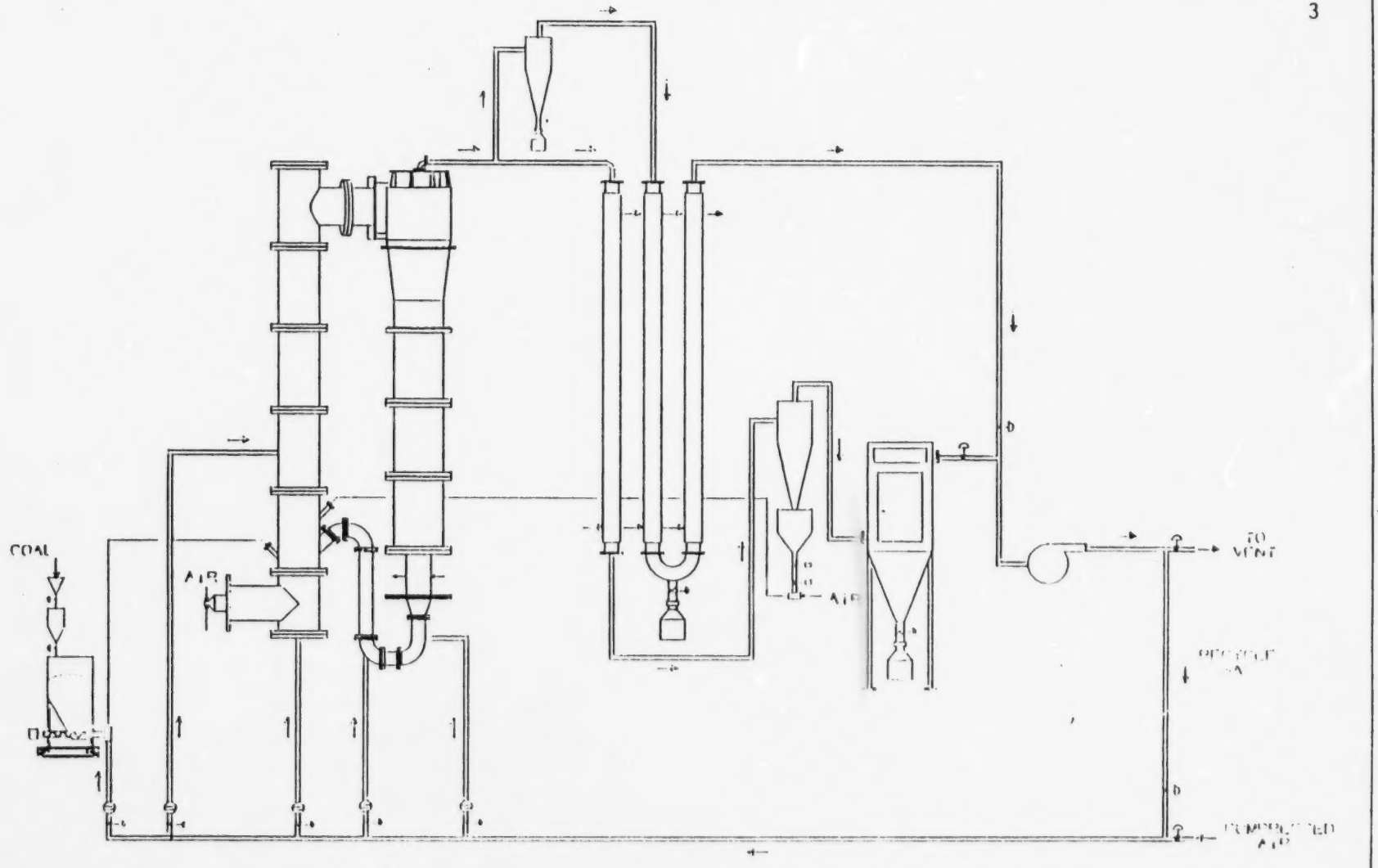


FIGURE 1 : SCHEMATIC OF RPC CYCLIC PYROLYSIS AND COMBUSTOR SYSTEM

2.2 Stand Pipe

The stand pipe is used for storage and recirculation of hot solids received from the primary cyclone. It is 2.7 m (9') high and has an inside and outside diameter of 22.8 cm (9") and 61 cm (24") respectively. The stand pipe is also refractory lined and it is also equipped with discharge and sampling ports.

2.3 Primary Cyclone

The primary cyclone which is 30 cm (12") in diameter, is refractory lined in a similar manner to the reactor and the standpipe.

2.4 J-Valve

Circulation of solids from the standpipe to the reactor is achieved by the non-mechanical J-valve. Air/recycle gas is supplied at two points - one at the base of the standpipe, and the other is at the base of the vertical section of the J-valve. The J-valve is made of 2", Schedule 40, SS pipe.

2.5 Combustion Cycle Off-Gas Cleaning

2.5.1 The Cooling Section

The gases were cooled in a water cooled one pass heat exchanger which is made of two concentric pipes of a nominal diameter of 15 cm (6") (Schedule 40) and 20 cm (8") (Schedule 60), respectively. The height of the heat exchanger is 5.2 m (17").

2.5.2 The Secondary Cyclone

The secondary cyclone is 25 cm in diameter and made of 304 SS stainless steel. Since the operating temperature is low, the cyclone is neither insulated or refractory lined.

2.5.3 The Baghouse

The flue gases from the cooling section are fed through the secondary cyclone into the baghouse. The latter is a continuous duty self cleaning dust collector which consist of 16 ft. high temperature bags capable of handling 200 SCFM.

2.6 Pyrolysis Cycle Off-Gas Cooling and Cleaning

2.6.1 Secondary Cyclone

The secondary cyclone is identical to that used on the combustion train. The cyclone performed satisfactorily and separated an appreciable amount of the dust from the off gases.

2.6.2 Packed Bed Condensers

The condensers are made of two concentric pipes of nominal diameter of 15 cm (Schedule 40) and 20 cm (Schedule 60). The inside pipe was filled with rasching rings up to a height of 4.85 m.

2.7 Solid Feeding to the Reactor

The solids, discharged by a screw feeder from a storage bin, were entrained by air/recycle gas and fed into the reactor. The storage bin is placed on a load cell to provide an account of the solid feed rate.

3.0 PREPARATION AND CHARACTERIZATION OF FEED STOCK

The size analysis, ultimate, proximate and ash analysis and the Fischer assay results are shown in Table 1, 2 and 3, respectively. Shale fines were prepared by screening dried as-received oil shale. The "shale fines from crushed shales" as shown in Table 1 were made by crushing the oversize fraction retained by $\frac{1}{4}$" screen. In the present program, all runs were made with the new shale fines (sample 1) and the fines generated from the crushed shale (sample 2).

TABLE 1
SIEVE ANALYSIS OF SHALE
FINES AND COAL

Screen Size Mesh(mm)	Weight % Shale Fines	Weight % Coal
+9 (2)	12.6	36.1
-9+24(0.71)	46.6	26.4
-24+42(0.35)	17.0	16.8
-42+80(0.18)	8.2	11.9
-80+ fines	15.6	8.8

TABLE 2
CHEMICAL ANALYSES OF OIL SHALES
AND MINTO COAL

	New Shale Fines (sample 1)	Shale Fines from crushed Shale (Sample 2)	Shale Fines from old Batch Sample 3	Minto Coal
Proximate Analysis (wt %)				
Moisture	1.93	1.74	1.00	0.52
Ash	82.27	79.50	81.49	14.1
Volatile Matter	16.00	18.50	18.00	35.5
Ultimate Analysis (wt %)				
Carbon - Organic	9.23	10.38	7.87	72.48
Inorganic	0.1	0.76	1.79	-
Hydrogen	1.77	1.81	1.40	4.92
Oxygen	0.42	0.45	0.39	0.93
Oxygen	4.13	5.05	5.78	1.4
Sulfur	0.25	0.31	0.28	5.70
Ash Analysis (wt %)				
SiO2	66.6	67.3	66.8	28.8
Al_2O_3	15.72	15.99	14.99	19.3
CaO	2.16	3.78	5.96	0.37
MgO	1.48	1.84	1.48	0.26
Fe_2O_3	6.68	4.64	5.61	48.7
Na_2O	1.93	2.00	1.50	0.41
K_2O	1.92	2.05	2.06	0.60
Calorific Value Btu/lb	1701	2026	1409	12844

TABLE 3
FISCHER ASSAY ANALYSES OF
OIL SHALE AND MINTO COAL

	New Shale Fines	Shale Fines From Crushed Shale	Shale Fines From Old Batch	Minto Coal
% Oil Yield	3.3	3.9	4.0	2.6
% Gas Lost	4.1	6.6	1.6	1.3
% Water Yield	1.6	2.5	3.4	1.1
Oil Yield (Imp Gal/Ton)	7.5	8.9	9.2	5.6
Oil Density (g/cc at 15.5°C)	0.875	0.870	0.871	0.919

4.0 EXPLORATORY HOT TESTS

4.1 Experimental Procedure

The circulating fluidized bed was started in the combustion mode which continued for several hours before the pyrolysis cycle was initiated. During the start-up only coal was used as a fuel. When the reactor temperature was over 800°C, the coal was replaced by 1:3 coal/oil shale mixture. Detail start-up procedure are as follows:

The standpipe was filled with 200 kg of sand prior to preheating of the combustor with a 0.5 million Btu/hr propane burner. When the temperature of the combustor was over 700°C, recycling of the sand from the standpipe was initiated. The standpipe was preheated by the hot recycling sand. Coal feeding was initiated when the standpipe temperature was over 600°C. Preheating of the combustor system took over twelve hours. Steady combustor operation was achieved in approximately 16 hours.

4.2 Process Performance

The system was operational for approximately 200 hours during two separate test runs. The first test lasted for about 100 hours, after which the system was shut down due to pressure build-up. Subsequent examination showed that the condenser columns were partially plugged with dust from the off-gas. In this test, both the primary and the secondary air streams were replaced by recycle gas during the pyrolysis cycle. Other streams of air which account for approximately 30% of total air supplied, were not replaced by the recycle gas. The rationale was that the recycle gas which carries residual oil mist (even after cleaning), could foul-up the flow meters and solid transport pipes.

In the first test, nine pyrolysis cycles were attempted. One pyrolysis cycle lasted for 43 minutes and another for 30 minutes. The remaining seven trials did not last for more than 15 minutes. The experimental conditions for the longest run are as follows:

Solid Feed Rate:	22 kg/hr
Coal/Oil Shale Mix:	1:3
Fluidizing Velocity:	6-7.5 m/s
Temperature on Initiation of Pyrolysis Cycle:	820°C
Temperature on Termination:	650°C
Duration of Pyrolysis Cycle:	43 minutes

Once bed temperature reached 650°C, the pyrolysis cycle was terminated and air was introduced to the reactor for the initiation of the combustion cycle. The feeding of coal shale mixture was not resumed immediately in order to allow the combustion of the accumulated char (from pyrolysis cycle), which raised the bed temperature to approximately 710°C. The bed was then brought up to the operating temperature (850 ± 20°C) by the introduction of fresh coal and oil shale.

The pyrolysis products collected at the bottom of the condenser column for all the trials consisted mainly of water mixed with carry over char. No detectable amount of oil was generated. It is believed that the failure to form oil products was due to the fact that air, which constituted approximately 30% of the fluidizing gas, combusted any oil generated during pyrolysis.

High dust loading in the product gas led to partial plugging of the gas cleaning system. This inturn, led to a reduction in the amount of the recycled gas which created a number of operational problems such as slugging, pressure fluctuation, erratic solid recycle and difficulties with the solid feeding system. For these reasons the test was terminated and subsequent examination confirmed that the plugging of the condenser pipes.

In the second series of tests which also lasted for approximately 100 hours, the problems of water formation and condensers plugging were addressed. The remaining air streams were replaced by the recycle gas to avoid the combustion of oil. Condenser plugging was remedied by spraying water at the top of the first condenser column so that dust and water would form sludge which could be removed at the bottom of the condenser column.

Ten attempts were made to initiate the pyrolysis cycle, but none of them was very successful. Despite the fact that enough gas could be recycled back into the reactor, it's distribution to the different streams proved to be difficult. A steady gas flow at a constant and sufficiently high pressure is necessary for the solid feeding, and for the operation of the J-valve for adequate solid circulation. Fluctuation in the pressure and flow rates, led to plugging of the solid feed line and also resulted in a erratic solid circulation. The latter is necessary in order to dilute the incoming feed stream and prevent clinker formation. Due to these difficulties and the lack of oil products, this series of tests were terminated after 100 hours of continuous operation.

4.3 Preliminary Gasification Tests

At the end of the second series of tests, gasification of 1:3 coal-shale mixture was attempted. Saturated steam was introduced between the primary and secondary air inlet as a gasification medium. The test was terminated after 3 hours when the condensers were plugged causing increased pressure inside the reactor. Also the product gas contained approximately 15-16% CO_2 and 3-4% CO. Temperature inside the reactor was approximately 800°C. Despite the short operational period, we are confident that the product gas quality can be improved significantly and the process can be made to operate reliably.

5.0 RECOMMENDATION FOR FUTURE WORK

Since the pyrolysis program was not quite as successful as anticipated, it is suggested that efforts be directed towards the gasification of coal-oil shale mixtures for the production of low Btu gas, which could be a viable option for the effective utilization of N.B. high sulfur coal and oil shale. The cost of production of such a gas is expected to be in the range of $4.00-$6.00 per million Btu.* Candidate industries for such gases in New Brunswick would include N.B. Power Commission, Pulp and Paper and the mining and mineral processing industries. From a technical point of view, a circulating fluidized bed gasification is expected to offer the following advantages.

- low sulfur and nitrogen level in the product gas
- minimal tar formation
- high carbon conversion efficiency

5.1 Tentative Work Statement

The primary objectives of this test program will be an assessment of the different operating parameters on the product gas quality and sulfur capture. The entire program can be divided into several tasks and sub-tasks as given below. It should be noted that feedstock preparation and characterization have already been carried out.

---

* Soriano, A.V., "Commercial Development of a Large Scale Coal Gasification System Designed to Produce Low Btu Gas"; Presented at the Eleventh Energy Technology Conference and Exposition, March 19-21, 1984; Washington, D.C.

Teper, M.; Hemming, D.F.; Ulrich, W.C., "The Economics of Gas from Coal", IEA Report by Economic Assessment Service, EAS Report E2/80, January, 1983.

Task 1: Test Program

- conduct test runs of 18 hours duration with a minimum of 12 hours at stable operating conditions as follows:

Set 1 Determine the Effect of C/H_2O Ratio on Carbon Conversion and Product Gas Quality

- use 1:1 coal-oil shale mix

- keep air and solid flow constant so that C/O_2 ratio remains constant. Set gas flow rate such that the operating velocity is 7 m/s

- set C/H_2O ratio at 0.5, 0.75, 1.0 and 1.25

Set 2 Determine the Effects of Coal/Oil Shale Mix on Product Quality.

- use the optimum C/H_2O ratio as determined in set 1, and with rest of the operating parameter as given above, carry out two tests using 1:2 and 1:3 oil shale/coal mixtures

Set 3 Determine the Effect of Temperature and C/O_2 Ratio on Product Quality

- use optimum C/H_2O ratio and oil shale and coal mixtures as determined in set 1 and 2

- vary C/O_2 ratio to attain three different temperatures such as 800^o, 850^o and 900^oC.

Set 4 Comparison with the Gasification Characteristics of Minto Coal

- carry a number of short tests to optimize product quality and carbon conversion. These test would not exceed 3 hours. Use as starting set of conditions the best C/H_2O and C/O_2 ratios as determined in sets 1 to 3.

- carry out an extended test at the optimum operating conditions

- compare the results with these obtained for coal oil shale mixture.

Measurements

The following measurements will be taken on hourly basis:

- feed rates of solid, gas and air, and the discharge rate of solids collected at different locations such as the standpipe and baghouse.

- temperatures of the reactor and standpipe, and at other strategic locations.

Sampling

Take the following samples periodically:

- samples of discharged solids from the system

- gas samples for analysis by GC

Analysis

- ultimate analysis and heating values of waste solid samples

- gas samples will be analyzed for H_2, CO, CO_2, N_2, CH_4, C_2H_4, H_2S, NH_3

- product gases will be monitored continuously by the on-line analyzers for CO, CO_2, O_2 and hydrocarbon

Task 2 Data Analysis

All runs will be evaluated in terms of carbon conversion, sulfur capture, thermal efficiency, steam decomposition and the heating values of the product gas. Also the effect of the various operating paramters on the process performed should be determined.

Task 3 Final Report

The final report will include:

- detailed description of the process

- description of operating procedures

- experimental results in tabulated and graphical forms

- discussions and interpretations of experimental results and recommendation for future work.

5.2 Budget and Schedule

The total budget for the pyrolysis contract is $98,191.00. The Crowns share is $54,655.00 and the balance is provided by the Provincial Government through Provincial Holdings Ltd. Expenditure to date is approximately $28,000. The remaining funds should be sufficient to carry out the gasification work described above and the projects could be completed 4 months after authorization.

AUTHORIZATION

DEPARTMENT: APPLIED SCIENCES

PROJECT TITLE: PYROLYSIS OF NEW BRUNSWICK OIL SHALE AND COAL IN A CIRCULATING FLUIDIZED BED

PROJECT NUMBER: 05000227 PROPOSAL NUMBER

REPORT AS/87/12

Prepared By: S.K. Barua

Reviewed By: P.Salib

Approved By:

Date: July 4, 1986

rpc RESEARCH AND PRODUCTIVITY COUNCIL
P.O. Box 6000, Fredericton, New Brunswick, Canada, E3B 5H1
Telephone (506) 452-8994
Telex 014-46115

APPENDIX 2

RESULTS OF CHEMICAL ANALYSIS

Analysis of Solid Waste Samples

ULTIMATE ANALYSIS (WT%)

Sample***	H_2O	Volatiles	Ash	C	H	N	S	O	Calorific Value (BTU/lb)
Run #1,Baghs.	0.82	13.0	0.97	41.51	3.42	0.76	51.18	1.34	6225
Run #1,SC	0.60	6.3	0.68	**52.01	5.18	0.22*	44.24	<0.1	7783
Run #1,Col.	0.36	2.9	0.58	41.67	1.27	0.16	55.97	<0.1	5873
Run #1,Bed.Mat.	<0.01	0.5	<0.01	1.00	0.85	0.12	99.26	<0.1	<100
Run #2,Baghs.	0.71	14.4	0.82	41.29	3.06	0.68	51.42	2.02	6266
Run #2,SC	0.66	8.0	0.60	44.76	1.03	0.28	53.09	<0.1	6488
Run #2,Col.	0.57	5.2	0.58	44.77	1.02	0.16	52.78	0.12	6274
Run #2,Bed.Mat.	<0.01	0.4	<0.01	0.28	0.85	0.04	100	<0.1	<100
Run #3,Baghs.	0.76	14.8	1.05	40.40	2.18	0.70	52.34	2.57	6280
Run #3,SC	0.78	6.9	0.55	40.45	1.11	0.22	56.77	0.12	5954
Run #3,Col.	0.44	4.0	0.46	43.70	1.17	0.14	58.42	<0.1	5571
Run #3,Bed.Mat.	<0.01	0.4	<0.01	1.16	0.21	0.07	98.64	<0.1	<100
Run #4,Baghs.	0.89	15.5	1.21	39.62	2.99	0.82	51.72	2.75	6770
Run #4,SC	0.50	6.8	0.64	47.09	1.86	0.18	50.17	<0.1	7058
Run #4,Col.	0.48	4.0	0.72	52.79	1.15	0.18	45.37	<0.1	7528
Run #4,Bed.Mat.	<0.01	0.5	<0.01	0.99	0.57	0.07	98.95	<0.1	<100
Run#5 Baghs	0.91		79.68	17.17	0.61	0.96	1.82	-1.15	2612
Run#5 Col.	<0.1		72.58	27.73	0.55	0.35	1.29	-2.50	3902
Run#5 SC	<0.1		77.36	22.64	0.43	0.31	1.16	-1.90	3342
Run#5 SPD	<0.1		91.41	9.13	0.27	0.13	0.66	-1.60	1178
Run#6 Baghs	0.58		81.11	15.47	0.64	0.72	2.15	-0.67	2442
Run#6 Col.	<0.1		80.62	20.05	0.46	0.23	1.38	-2.74	2760
Run#6 SC	<0.1		79.54	20.74	0.36	0.36	1.36	-2.36	2696
Run#6 SPD	<0.1		86.41	14.05	0.27	0.30	0.99	-2.02	1593
Run#7 Baghs	0.52		83.60	14.56	0.57	0.35	1.42	-1.02	1722
Run#7 Col.	<0.1		79.48	20.49	0.29	0.35	1.42	-2.03	3025
Run#7 SC	<0.1		79.83	20.06	0.52	0.37	1.17	-1.95	2795
Run#7 SPD	<0.1		92.49	8.14	0.24	0.18	0.76	-1.81	1161

Table 2 Results (w/w%) as received basis.

Sample***	H_2O	Volatiles	Ash	C	H	N	S	O	Calorific Value (BTU/lb)
Run#8 Baghs	0.11		89.83	9.68	0.41	0.31	0.96	-1.30	1394
Run#8 Col.	<0.1		82.96	17.45	0.31	0.26	1.27	-2.25	2578
Run#8 SC	<0.1		87.75	12.90	0.42	0.23	1.02	-2.32	1935
Run#8 SPD	<0.1		89.00	11.48	0.21	0.19	0.83	-1.71	1653
Run#8 Bed	3.66		95.42	0.79	0.18	0.11	0.23	-0.39	<100
Run#9 Baghs	<0.1		93.24	6.39	0.42	0.24	0.75	-1.04	873
Run#9 Col.	<0.1		91.49	8.75	0.23	0.18	1.09	-1.74	1244
Run#9 SC	<0.1		91.49	8.62	0.29	<0.1	0.93	-1.33	1232
Run#9 SPD	<0.1		91.52	9.23	0.26	<0.1	1.10	-2.11	1332
Run#10 Baghs	<0.1		83.89	13.81	0.49	0.58	1.62	-0.39	2011
Run#10 Col.	<0.1		77.41	22.48	0.36	0.33	1.51	-2.09	3290
Run#10 SC	<0.1		80.85	21.53	0.45	0.27	1.32	-4.42	2809
Run#10 SPD	<0.1		85.84	14.17	0.23	0.23	1.00	-1.47	1999
Run#11 SPD	5.00		0.10	1.28	<0.1	96.58	0.33	<0.1	720
Run#11 Baghs	12.49		0.41	1.05	<0.1	87.58	0.36	<0.1	1899
Run#11 Col	14.28		0.22	1.20	<0.1	87.24	0.27	<0.1	2058
Run#11 Cyc	14.39		0.27	1.14	<0.1	86.71	0.23	<0.1	2140
Run#11 Bed.Mat	0.74		0.16	trace	0.96	<0.1	99.94	<0.1	74

Note: The apparent deficiency of oxygen is attributed to changes in the chemical composition of the material during ashing.

** 50.61 (by Leco) * Repeat: 44.23%

*** Baghs. - Baghouse
SC - Secondary Cyclone Discharge
Col. - Column Discharge
Bed.Mat. - Bed Material Sample from J-Valve
SPD - Standpipe Discharge (Bed Overflow)

APPENDIX 3

SUMMARY OF WEEKLY ACTIVITIES

The gasifier was operational for a total of 32 days spread over eight weeks. The first five weeks were spent debugging the system so that it could be operated reliably for an extended period of time. Among the major equipment malfunctions were blower failure, and an unsatisfactory performance by the baghouse. Slugging, feed disruption and unreliable recycling were the major operational problems encountered.

The activities and the problems encountered and their solutions are summarized on a weekly basis.

First Week:

The major operational problem for the first week was created by the condensation of water vapor in the flow gases at the bottom of the condenser column and in the baghouse. This caused, pressure build up in the system creating problems such as the disruption in the coal feed and unreliable solid recycle from the standpipe resulting in the clinker formation. The condensation of water vapor in the condenser column was avoided by turning off the cooling water and in the baghouse by heat tracing the inlet of the baghouse. These arrangements were found to be satisfactory.

Second Week:

During this period, there was a consistent problem of slugging in the combustor. Slugging is undesirable because it reduces the heat and mass transfer rates. It also creates pressure fluctuation in the system which tended to plug the coal feed line and reduced the reliability of the solid recycle from the standpipe. To avoid slugging the solid recycle was set to minimum by reducing the aeration and lift air. Although slugging was reduced it was not eliminated.

The run was terminated due to disruption in solid recycle which was caused by the presence of small lumps in the J-valve. The following week was devoted to solving the problem of lump formation.

Third Week:

These small lumps which were responsible for the disruption of the recycling were porous, soft and light which suggests that they were not formed by the fusion of ash. Rather, they were formed by the agglomeration of coal, from which volatiles had been expelled leaving a partial coke. A screen was placed at the bottom of the cooling section to prevent them entering the J-valve and blocking it. To avoid the formation of these lumps the steam was injected further above the coal feed port so that the coal was subjected to an oxidizing atmosphere to reduce its agglomeration tendencies.

The gasifier was shut down when the clinker was formed in the J-valve. Upon examination it became evident that the clinker in the J-valve was due to the combustion of accumulated char in the standpipe, ie. it was formed in the stand pipe rather than in the reactor itself. Table 4 shows the accumulation of char in the standpipe.

TABLE 4

Accumulation Char in the Standpipe

Hours of Operation	% Combustibles
19	0.73
23	1.42
35	3.22
40	8.48

Fourth week:

To eliminate the combustion of char in the J-valve, aeration air was replaced by steam/water. This has the advantages of preventing combustion and ash fusion in the J-valve and it leads to higher steam residence time for increased gasification reactions.

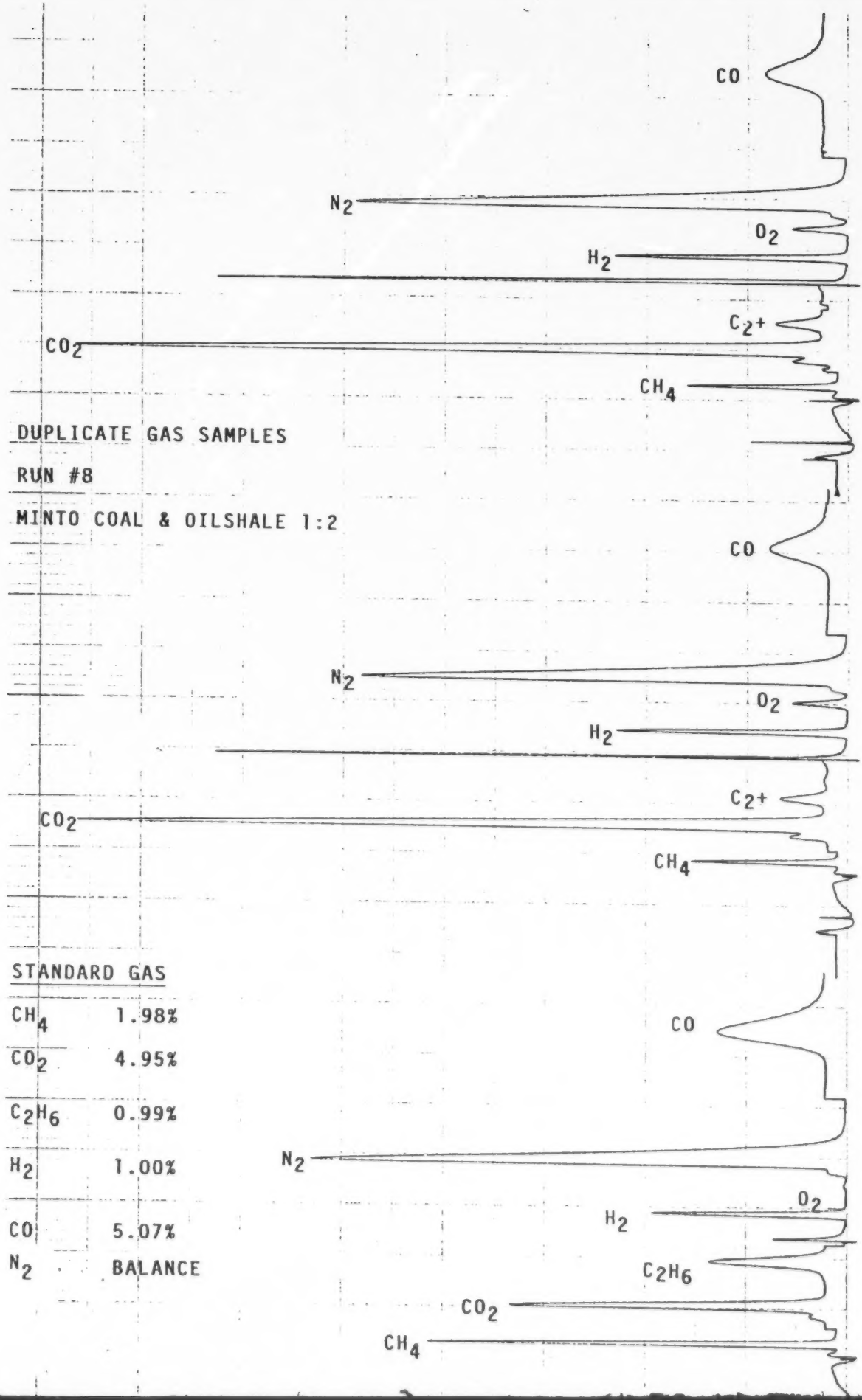
The amount of steam required for aeration is much lower than the C/H_2O ratio necessary for the gasification reaction. Therefore only a part of the total steam requirement was injected as aeration gas at the J-valve. The remaining steam was injected in the reactor. Although the formation of clinker was avoided, aeration of the J-valve by steam was unsatisfactory with frequent interuption in solid recycle. In absence of solid recycle led to clinker forms in the reactor. As a result of the discontinuous recycle temperature in the combustor fluctuated considerably (840-890^{o}C) so did the system pressure. The latter led to solid feeding difficulties. Therefore, it was decided to introduce a mixture of air and water/steam as a aeration gas. Water air ratio of 1 ml: 0.067 SCF performed satisfactorily.

Fifth Week:

The problem of slugging in the reactor persisted as evident from the wide variation of temperature in the combustor. Finally, the problem of slugging was solved by increasing the primary air from 28 scfm to 36 scfm. No further slugging was encountered.

Pressure drop across the baghouse showed marked increase, although cleaning of the bags helped somewhat, the problem could not be eliminated. It was resolved by diverting a portion of the gas to bypass the baghouse and replacing some of the bags with the new ones.

In the following three weeks, all the experimental runs were made and no major equipment failures or operational difficulties were encountered.


CO
N2
O2
H2
C2+
CO2
CH4
DUPLICATE GAS SAMPLES
RUN #8
MINTO COAL & OILSHALE 1:2
CO
N2
O2
H2
C2+
CO2
CH4
STANDARD GAS
CH4 1.98%
CO2 4.95%
C2H6 0.99%
H2 1.00%
CO 5.07%
N2 BALANCE
CO
N2
O2
H2
C2H6
CO2
CH4